PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 7:

C10G 7/00, 73/42

(11) International Publication Number:

WO 00/11113

(43) International Publication Date:

2 March 2000 (02.03.00)

(21) International Application Number:

PCT/IB99/01448

A1

ZA

(22) International Filing Date:

19 August 1999 (19.08.99)

(30) Priority Data:

98/7599

21 August 1998 (21.08.98)

135, CH-1264 St. Cergue (CH).

2158 (ZA). ROZA, Mario [NL/CH]; Chesaux Dessus D4,

(74) Agent: KOTZE, Gavin, Salomon; Adams & Adams, Adams & Adams Place, 1140 Prospect Street, Hatfield, 0083 Pretoria

(71) Applicants (for all designated States except US): SCHU-MANN-SASOL (SOUTH AFRICA) (PROPRIETARY) LIMITED [ZA/ZA]; 1 Sturdee Avenue, Rosebank, 2196 Johannesburg (ZA). SULZER CHEMTECH LIMITED [CH/CH]; Hegifeldstrasse 10, CH-8404 Winterthur (CH).

(72) Inventors; and

(75) Inventors/Applicants (for US only): OLIVIER, Anthony, John [ZA/ZA]; 14 Wagner Street, Sasolburg 9570 (ZA). RICHTER, Ferdinand [DE/DE]; Duesterntuiete 56, D-22549 Hamburg (DE). DUCKITT, Charles [ZA/ZA]; 34 Wagner Street, Sasolburg 9570 (ZA). RAMDUTH, Ashwin [ZA/ZA]; 14 Christerlo Heights, Karas Street, Vaalpark, Sasolburg 9573 (ZA). ADAMS, Vernon, Jeremay [ZA/ZA]; 8A Acacia Flats, Sasolburg 9570 (ZA). MOODLEY, Vinothen [ZA/ZA]; D41 The Lofts, Boland Park, Louis Fourie Street, Mossel Bay 6500 (ZA). CALDER, Roy, Alexander [GB/ZA]; 9 Mispel Street, Sharonlea, Randburg

(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES. FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

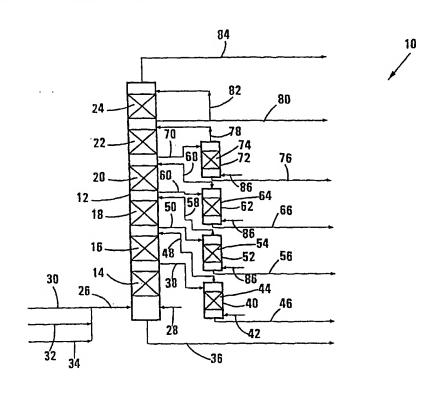
Published

With international search report.

(54) Title: PROCESS FOR DISTILLING FISCHER-TROPSCH DERIVED PARAFFINIC HYDROCARBONS

(57) Abstract

A process for distilling paraffinic hydrocarbons comprises feeding a Fischer-Tropsh derived paraffinic hydrocarbon feedstock comprising heavy paraffinic hydrocarbons and, optionally, light and/or medium paraffinic hydrocarbons, into a distillation column. The distillation column is operated to produce usable wax products. An overhead stream, a bottom stream, and at least one side stream, are withdrawn from the distillation column. All the wax products obtained are usable wax products.



FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
ΑZ	Azerbaijan	GB	United Kingdom	MC	Мопасо	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav	TM	Turkmenistan
BF	Burkina Faso	GR	Greece		Republic of Macedonia	TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	zw	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's	NZ	New Zealand		
CM	Cameroon		Republic of Korea	PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SÉ	Sweden		
EE	Estonia	LR	Liberia	SC	Singapore		

10

15

20

25

PROCESS FOR DISTILLING FISCHER-TROPSCH DERIVED PARAFFINIC HYDROCARBONS

THIS INVENTION relates to distillation. More particularly, the invention relates to a process for distilling paraffinic hydrocarbons, particularly Fischer-Tropsch derived paraffinic hydrocarbons.

According to the invention, there is provided a process for distilling paraffinic hydrocarbons, which process comprises feeding a Fischer-Tropsch derived paraffinic hydrocarbon feedstock comprising heavy paraffinic hydrocarbons and, optionally, light and/or medium paraffinic hydrocarbons, into a distillation column;

operating the distillation column to produce usable wax products; and

withdrawing from the distillation column an overhead stream, a bottom stream comprising usable wax products, and at least one side stream comprising usable wax products.

The usable wax products are thus Fischer-Tropsch derived. Fischer-Tropsch derived wax products must usually meet stringent specifications for several properties or characteristics. Some of the more important of such properties or characteristics are the congealing point, softness at various temperatures (measured by needle penetration), oil content (measured by the wax product solubility in methyl-ethyl-ketone (MEK) or methyl-isobutyl-ketone (MIBK) solvents) and olefin content (measured using

hereinbefore set out.

5

10

15

20

25

30

a bromine index). Also of importance are DSC (Differential Scanning Calorimetry) curves (these are 'finger prints' of wax showing the energy absorption as a function of temperature) and GPC (Gel Permeation Chromatography) data. GPC data are a measure of molecular weight, the heavy tail

2

By 'usable' in respect of the wax products is meant that the wax products are non-thermally degraded. products will also meet the stringent specifications of some or most of the properties or characteristics

and the light ends that are present in a wax.

By 'Fischer-Tropsch derived' in respect of the paraffinic is meant paraffinic products feedstock, obtained by subjecting a synthetic gas comprising carbon monoxide (CO) and hydrogen (H2) to Fischer-Tropsch reaction conditions in the presence of an iron-based, a cobalt-based or an iron/cobalt-based Fischer-Tropsch catalyst.

Prior to using the products from the Fischer-Tropsch reaction as a feedstock for the present process, they may optionally be hydrogenated. Such hydrogenation may be effected by contacting the Fischer-Tropsch reaction products with hydrogen in the presence of a hydrogenation catalyst, at elevated temperature and pressure, in known fashion.

Fischer-Tropsch derived wax products are unique since they are predominantly n-paraffinic with a wide boiling range. Some isomers, olefins, oxygenates and other functional groups may also be present. The high n-paraffinic content of Fischer-Tropsch waxes enables them to meet the stringent hereinbefore referred to. specifications degradation, even in its mildest form of less than 2%, will cause an increase in isomer and olefin content which may immediately render the wax product non-usable.

10

25

30

The Fischer-Tropsch reaction conditions include using a relatively low reaction temperature in the range 180-300°C, typically 210-260°C, so that a so-called low temperature Fischer-Tropsch synthesis is employed, and the Fischer-Tropsch reaction is typically effected in a fixed or slurry bed reactor.

The feedstock may comprise, in addition to the heavy paraffinic hydrocarbons, the light and the medium paraffinic hydrocarbons. The feedstock could thus typically have a true boiling point curve as indicated in Table 1:

TABLE 1: True boiling point (TBP) curve of a typical Fischer-Tropsch derived feedstock

	Mass %	TBP (°C)
	1	142
15	5	169
	10	195
	30	313
	50	417
	70	550
20	90	716
	95	757
	98	831

The feedstock typically comprises hydrocarbon molecules in the range C_{3+} to C_{220+} . Products with carbon ranges of C_{35-} , C_{10} to C_{80} , and C_{15} to C_{220} or higher, are deemed light, medium and heavy hydrocarbons respectively.

The distillation column can be operated to produce paraffins (C_{23-}) , medium wax $(C_{20}$ to $C_{38})$, and hard wax (C_{30+}) or combinations thereof. All the wax products produced will thus be usable wax products as hereinbefore defined.

Preferably, however, a plurality of side streams are withdrawn from the column, with each side stream comprising

a component of the medium wax and/or a component of the hard wax, and, optionally, a component of the paraffins.

The distillation column is preferably operated under vacuum. Operation under vacuum permits a n-paraffinic hydrocarbon to boil at a lower temperature as compared to at atmospheric pressure. The lower temperature decreases, if not eliminates, thermal degradation of the feedstock and the products.

5

10

15

20

25

30

The distillation column may be operated such that the pressure in the column is in the range of 1 to 12 mbar(a), typically from 8-10 mbar(a). The temperature in the column sump may then be in the range of 190°C to 350°C, typically in the range of 295°C to 350°C.

The process may include feeding stripping steam into the distillation column, to adjust the relative volatility of components in the feedstock. The process may also include feeding one or more of the side streams through a stripping stage. It is envisaged that steam stripping can be used to adjust the front end volatility of the products, thereby to aid in product quality.

The distillation column will thus have a suitable internal arrangement. The internal arrangement may comprise trays or packing as distillation media. However, for vacuum distillation applications, the pressure drop over the required number of theoretical stages should be minimized to prevent or inhibit thermal degradation of distilled products. Additionally, packing generally results in lower pressure drops than trays for the same number of theoretical stages and the same vapor/liquid traffic in the distillation column. According to Distillation Design, by Henry Z. Kister, McGraw Hill, 1992 (hereinafter also referred to as 'Kister'), a vacuum distillation column with ten theoretical stages and operating at a 1 psi (about

5

70 mbar) top pressure, has a bottom pressure of 2,5 psi (about 175 mbar) when fitted with trays; however, the bottom pressure is only 1,4 psi (about 100 mbar) when it contains packing.

Packing is thus preferred as distillation medium. 5 packing may be random or dumped packing, ie, according to Kister, discrete pieces of packing of a geometrical shape and which are dumped or randomly packed into the column; structured or systematically arranged packing, ie, according to Kister, crimped layers of wire 10 mesh or corrugated sheets, with sections of such packing then being stacked in the column; and grid packing, ie, according to Kister, systematically arranged packing, but having an open-lattice structure rather than being in the form of wire mesh or corrugated sheets. The preferred 15 internal arrangement comprises structured packing, in view of its superior balance of efficiency, capacity and compared the other packings pressure drop as to hereinbefore described.

The structured packing may have a surface area (in m²) to volume (in m³) ratio of 125:1 to 750:1, e.g. 250:1, 350:1 or 500:1, or any other intermediate value.

25

30

As indicated hereinbefore, a plurality of the side streams may be provided, with the distillation column including a draw point or zone for each of the side streams as well as for the overhead and bottom streams, and with a plurality of distillation stages being provided in the distillation column, with each stage being located between the draw points or zones for two of the streams. Each stage may thus comprise the structured packing.

This packing and column internal arrangement produces a very low pressure drop and decreases entrainment while ensuring that the required separation is achieved. This

10

15

30

low pressure drop permits the addition of more column side draws or theoretical stages than would be the case if different column internals with higher pressure drops were to be used.

Typically, five theoretical stages are provided per bed of packing, with the respective beds each containing the packing and the internal arrangement, and each bed being located between draw points for the overhead, side and bottom streams from the column. The packings of the various beds and stages can have the same surface area to volume ratios, or the surface area to volume ratios of the packings of at least some of the beds and/or stages can be different. The internal arrangement minimizes the residence time within the distillation column, thus reducing the amount of thermal cracking of the products produced.

The process of the invention thus employs multiple side streams with separation stages in the column between the withdrawal of the side streams, to split wax fractions.

Thermal degradation can be further countered by cooling down the bottom stream, and recycling a small proportion, typically less than 10% by volume, of the cooled bottoms product to the column sump to quench the sump content. This can be done without appreciably effecting the front end cut of the column bottoms product or the tail end of the column side stream or draw-off immediately above the column bottoms product, ie the stringent specifications hereinbefore referred to can still be met.

With the process of the invention, the Fischer-Tropsch derived feedstock is thus fractionated into product streams having unique properties or characteristics. One of these properties is the congealing point, which can thus be used to control the operation of the distillation column.

10

15

20

25

30

WO 00/11113 PCT/IB99/01448

7

However, instead, or additionally, other unique properties. such as methyl-ethyl-ketone (MEK) and/or methyl-isobutylketone (MIBK) solubles (also referred to as the oil content), penetration at a particular temperature, which is in the range of 25°C to 60°C, distributions, etc. can be used to control distillation operation. The number of side streams from the column are determined by the properties of the products and by-product purity desired. There is, in principle, no restriction on the maximum number of side stream product draws other than the fact that the accumulated pressure drop of the internals must be limited.

It was surprisingly found that with the unique process according to the invention, Fischer-Tropsch feedstocks can be distilled into usable wax products in a single column that has one or more side streams. The use of the low pressure drop internals, stripping stream and/or the quenching of the contents of the column sump using cooled column bottoms product, inhibits or counters thermal degradation of the usable wax products.

The invention will now be described by way of example, with reference to the accompanying drawing and non-limiting example.

In the drawing, reference numeral 10 generally indicates, in simplified flow diagram form, a process according to the invention for distilling paraffinic hydrocarbons.

In the drawing, reference numeral 10 generally indicates a process according to the invention, for distilling a Fischer-Tropsch derived light, medium and heavy paraffinic hydrocarbon feedstock.

The process 10 includes a distillation column 12 having six vertically staggered packing stages 14, 16, 18, 20, 22 and

10

15

20

25

WO 00/11113 PCT/IB99/01448

8

Each packing stage comprises high performance structured packing and associated internals such structured packing having a surface area (in m2) to volume (in m³) ratio of 125:1, 250:1, 350:1, 500:1 or 750:1, or any appropriate intermediate value.

A feed line 26 leads into the bottom of the distillation column 12, as does a stripping steam feed line 28. the line 26 leads a light (C_{20}) hydrocarbon line 30, a medium $(C_{10} - C_{40})$ hydrocarbon line 32 and a heavy $(C_{15} -$ C₂₂₀₊) hydrocarbon line 34.

The feed line 26 and the stripping steam feed line 28 lead into the column below the lowermost packing stage 14.

A bottoms line 36 leads from the bottom of the column 12.

A side stream line 38 leads from the column between the packing stages 14, 16 to a stripping column 40, with a stripping steam line 42 leading into the bottom of the The column 40 comprises a packing stage 44 comprising sieve trays. A product line 46 leads from the bottom of the column 40, while a return line 48 leads from the top of the column 40. The return line 48 returns to the column 12 between the packing stages 16, 18.

stream withdrawal line 50 leads distillation column between the packing stages 16, 18 into a stripping column 52 having a packing stage 54 comprising sieve trays. A product withdrawal line 56 lead from the bottom of the column 52, while a return line 58 leads from the top of the column 52 back to the distillation column 12 between the packing stages 18, 20.

A side stream withdrawal line 60 leads from the column 12 between the packing stages 18, 20. The line 60 leads into 30 the top of a stripping column 62 having a packing stage 64

20

25

comprising sieve trays. A product withdrawal line 66 leads from the bottom of the column 62, while a return line 68 leads from the top of the column 62 back to the distillation column 12 between the packing stages 20, 22.

A side stream withdrawal line 70 leads from the distillation column 12 between the packing stages 20, 22. The line 70 leads into a stripping column 72 having a packing stage 74 comprising sieve trays. A product withdrawal line 76 leads from the bottom of the column 72, while a return line 78 leads from the top of the column 72 back to the distillation column 12, between the packing stages 22, 24.

A side stream/product withdrawal line 80 leads from the distillation column 12 between the packing stages 22, 24, and is fitted with a recycle line 82 returning to the distillation column 12 above the packing stage 24.

An overheads line 84 leads from the top of the column.

In use, a Fischer-Tropsch derived light, medium and heavy hydrocarbon feedstock is fed, along the flow line 26, into the bottom of the distillation column 12. The distillation column 12 is typically operated at a pressure of 8-10 mbar(a) and at a temperature, measured in the column sump, of about 295-300°C.

Usable wax products, such as medium wax $(C_{20} - C_{38})$ and hard wax (C_{30+}) are produced in the column 12.

The products withdrawn along the lines 36, 46, 56, 66, 76, 80 and 84 typically comprise C_{35+} , C_{25} - C_{40} , C_{20} - C_{30} , C_{19} - C_{23} , C_{18} - C_{20} , C_{17-} and C_{5-} respectively.

Stripping steam lines 86 lead into the bottoms of each of these stripping columns 52, 62, 72.

10

The following non-limiting examples were also conducted, in simulations of the process 10:

EXAMPLE 1

5

10

15

The feedstock entering the column 12 along the line 26 comprised light hydrocarbons (also known and referred to as Cold Condensate (CC)), medium hydrocarbons (also known and referred to as Hot Condensate (HC)) and heavy hydrocarbons (also known and referred to as Reactor Waxes (RW)). All the hydrocarbons were Fischer-Tropsch derived. Thus, each component of the feedstock was a blend of the respective products from both fixed and slurry bed reactor Fischer-Tropsch processes. The blend ratio (mass basis) in this example was:

CC = 28,8% HC = 17,2%

RW = 54,0%

The number of side streams from the column 12 are determined by the properties of the product or the by-product purity desired.

There is no restriction on the maximum number of side product streams other than the fact that the accumulated pressure drop of the internals must be limited. If unlimited, energy loss and thermal cracking can be so significant that the process becomes technologically and/or economically non-viable.

Table 2 hereunder shows the streams produced, the desired congealing point (CP) range and typical CP values obtained.

11

TABLE 2

	Product	Name	CP Desired Range (°C)	Typical CP obtained (°C)	Carbon No Range
Overhead Stream 84	C ₅₋	Gas	n/a	n/a	5 max
Stream 80	C ₁₇₋	C ₁₇ -Paraffins	n/a	n/a	4-18
Stream 76	C ₁₈ -C ₂₀	C ₁₈ -C ₂₀ Paraffins	25-30	28	17-21
Stream 66	C ₁₉ -C ₂₃	Waksol	35-40	38	18-24
Stream 56	C ₂₀ -C ₃₀	Medium Wax 1	50-55	53	19-30
Stream 46	C ₂₅ -C ₄₀	Medium Wax 2	60-65	64	25-40
Bottom Stream 36	C ₃₅₊	Hard Wax	65 +	98	35-220

The yield of the above streams on a mass basis as a percentage of the feed was approximately:

	Overhea	ad Strea	am 84	=	. 1,0%
	Stream	80		=	27,6%
15	Stream	76		=	5,8%
	Stream	66		=	4.5%
	Stream	56		=	6,9%
	Stream	46		=	11,4%
	Bottom	Stream	36	=	42.8%

5

10

20

25

The column 12 was operated at a head pressure of 5 mbar(a) using a three stage steam ejector for its vacuum system. The pressure drops achieved over the 6 beds of structured packing was 25 mbar. Each bed of packing comprised Mellapak 250Y (trade mark) packing available from Sulzer Chemtech Ltd, PO Box 65, CH-8404, Winterthur, Switzerland. Some side streams had side stripper columns as indicated in the drawing. Low pressure (2,4 bar_g) steam was injected into both the bottom of the main fractionator and the side stripper columns to aid in separation.

12

EXAMPLE 2

5

The feedstock entering the column 12 along the line 26 had the following composition:

RW = 79% by mass HC = 21% by mass

The products obtained are given in Table 3.

TABLE 3

		TODE	GAS	GAS C5-	C17-PARAFFINS	AFFINS	WAXY OII	OIL
ANALYSES	UNITS	METHOD	Spec	Typical	Spec	Typical	Spec	Typical
Congealing Point	၁့	ASTM938					26-30	28
Cloud Point	၁့	SASOL			•		•	1
Penetration at 25°C 40°C 65°C	0,1mm 0,1mm 0,1mm	ASTM D1321 ASTM D1321 ASTM D1321				1 4 4		1 1 4
MEK Solubles	mass %	ASTM D721	•	•	•	•	22 max	15
MIBK Solubles	mass %	ASTM D721			•	•	•	,
Saybolt Color (ASTM)	•	ASTM D156	,	•	•	1	+ 10 min	+20
Bromine Index	g Br/100g	SASOL	'	•	-	,	10 max	7
DSC Analyses: Melt range Maximum Fusion Enthalpy	၁ ့ ၆/Γ	SASOL						
GPC Analyses: Mn Mw Mz Pd	Daltons Daltons Daltons Daltons	SASOL				. ,		276 272 278 10
ASTM D2887 Data: 1BP 5% 55% 95% FBP	ဂ်ဂ်ဂ်ဂ်	ASTM D2887			1111	187 258 293	280 ⁻ 300 355-375	2 . 3228 3638 3638
Carbon Distribution: Range Peak > C 1 7 Iso-paraffins	C number C number mass % mass %	SASOL			4-18 12-13 0,15max	5-18 13 0,1		13-23

Table 3/.....cont

ont)	
<u>ဗ</u>	
က	١
Ш	l
ō	ļ
≤	l

		1551	MEDIUM WAX 1	+ 2 BLEND	HARD WAX	ΑX
ANALYSES	UNITS	METHOD	Spec	Typical	Spec	Typical
Congealing Point	၁့	ASTM938	56-60	57	96-100	97
Cloud Point	J.	SASOL	72 max	62		•
Penetration at 25°C 40°C 65°C	0, 1mm 0, 1mm 0, 1mm	ASTM D1321 ASTM D1321 ASTM D1321	24-32 120-130	26 128	1 max 25 max	<1 > 20
MEK Solubles	mass %	ASTM D721	3,2-4,2	4,0		•
MIBK Solubles	mass %	ASTM D721		ı	1,5max	0,8
Saybolt Color (ASTM)		ASTM D156	+ 10min	+20	+ 15min	+17
Bromine Index	g Br/100g	SASOL	1max	0,5	1max	<0.1
DSC Analyses: Melt range Maximum Fusion Enthalpy	, ° , ′	SASOL	3-7/58-63 53-56 180-189	6/60 54 188	19-22/111-114 76-78/100-102 228-237	21/112 77/101 232
GPC Analyses: Mn Mw Mz Mz Pd	Daltons Daltons Daltons Daltons	SASOL	351-379 363-391 370-398 1,0-1,1	365 372 1,0	636-664 799-827 1120-1148 1,2max	650 813 1134
ASTM D2887 Data: IBP 5% 50% 95% FBP	ပ္ပံပ္ပံပ္	ASTM D2887	345-365 485-505	356 412 490	465-485	475 636 819
Carbon Distribution: Range Peak > C17 Iso-paraffins	C number C number mass % mass %	SASOL	8max	19-40	4max	30-220
Product Yields: (mass %)	Gas C5- C17- Paraffins Waxy Oil	=0,1 affins =5,1 = 11,8		a x	1 for Blend = 12.7 2 for Blend = 12.7 = 57,6	

15

The column sump temperature was 300°C, and the head pressure was 5 mbar(a). The pressure drop achieved over the six beds of Mellapak 250Y packing was 15 mbar(a). All wax products met the stringent specifications for Fischer-Tropsch products and were consequently usable, as indicated in Table 3 above.

EXAMPLE 3

5

The feedstock entering the column 12 along line 26 had the following composition:

HC = 21% by mass

RW = 79% by mass

The products obtained are given in Table 4.

TABLE 4

I ABLE 4	GAŞ C5- C17-PARAFFINS WAXY OIL	HOD Spec Typical Spec Typical Spec Typical	м938 26-30 28	- 10S	D1321	D721 22 max 15	10721	1 D156 +10 min +20	SOL 10 max 7	SOL	SOL 276 272 272 278 278 278 278 278 278	D2887	SOL 4-18 5-18 - 13-23
	C17-		•	-	1	-		-	,	1 1 1			4-18
DLE 4	45 C5-				, , ;	-	1					1 1 1 1	
H H	/9	Spec	·				Eq. (•				
	7507	METHOD	ASTM938	SASOL	ASTM D1321 ASTM D1321 ASTM D1321	ASTM D721	ASTM D721	ASTM D156	SASOL	SASOL	SASOL	ASTM D2887	SASOL
		UNITS	၁့	၁့	0, 1mm 0, 1mm 0, 1mm	mass %	mass %	•	g Br/100g	ပ္ပင္	Daltons Daltons Daltons Daltons	ပ်ပိုပ်ပို	C number C number
		ANALYSES	Congealing Point	Cloud Point	Penetration at 25°C 40°C 65°C	MEK Solubles	MIBK Solubles	Saybolt Color (ASTM)	Bromine Index	DSC Analyses: Melt range Maximum Fusion Enthalpy	GPC Analyses: Mn Mw Mz Mz Pd	ASTM D2887 Data: 1BP 5% 55% 958% FBP	Carbon Distribution: Range Peak

Table 4/....cont

_
₽
0
ပ္ပ
_
4
ш
ائب
띪
₹
\succeq

			1001 - 3000	/1.1				
		} C }	MEDIUM WAX 1 +	AX 1 + 2	MEDIUM WAX 3	WAX 3	HARD WAX	×
ANALYSES	UNITS	METHOD	Spec	Typical	Spec	Typical	Spec	Typical
Congealing Point	၁့	ASTM938	26-60	58	74-78	76	97-100	66
Cloud Point	၁့	SASOL	72 max	65	85тах	82		,
Penetration at 40°C 65°C	00,1mm 0,1mm 1mm 1mm	ASTM D1321 ASTM D1321 ASTM D1321	24-32 120-130	26 126 -	15max	14	1max 19max	<1 - 13
MEK Solubles	mass %	ASTM D721	3,2-4,2	3,9	15max	1,3		
MIBK Solubles	mass %	ASTM D721	ţ	•	•	•	1,0max	0,4
Saybolt Color (ASTM)		ASTM D156	+ 10min	+ 19	+ 10min	+17	+ 10min	+14
Bromine Index	a Br/100a	SASOL	1max	0,5	1max	0,4	0,5max	0,2
DSC Analyses: Melt range Maximum Fusion Enthalpy	, , <u>, ,</u>	SASOL	3-7/58-63 53-56 180-189	6/63 54 188		21-78 67 205	30-34/113-118 84-88/102/107 230-240	33/117 86/105 235
GPC Analyses: Mn Mw Mz Mz	Daltons Daltons Daltons Daltons	SASOL	351-379 363-391 370-398 1,0-1,1	365 377 384 1,0		448 463 477 1,0	740-770 910-940 1208-1238 1.2max	755 925 1223 1.1
ASTM D2887 Data: 1BP 5% 50% 95% FBP	ပိုင်ပိုင်	ASTM D2887	345-365 485-505	359 420 - - -	460-480	469 595	530min -	540 676 830
Carbon Distribution: Range Peak > C17	C number C number mass %	SASOL		19-41	,	30-55		45-220
Product Vields: (mass %)	Gas C5- C17- Paraffins Waxy Oil	= 0, 1 affins = 5, 1 = 11, 8	Ollida	Medin	Medium Wax 1 for Medium Wax 2 for Medium Wax 3 for	r Blend r Blend	4max = 14,2 = 14,2 = 9,3	3,0
				Hard	Wax		= 45,3	

18

The column sump temperature was 330° and the head pressure was 5 mbar(a). The pressure drop achieved over the six beds of Mellapak 250Y packing was 15 mbar(a). All the wax products met the stringent specifications for Fischer-Tropsch products and were consequently usable, as indicated in Table 4 above.

5

10

The process 10 permits a light, medium and heavy Fischer-Tropsch derived feedstock to be distilled into normal usable product ranges using a single column with multiple product side streams. This has hitherto not been possible due to high pressure drops associated with conventional packing used in distillation columns. The wax products produced are usable wax products.

The process 10 is capable of producing a wide range of narrow cuts, and also has substantial flexibility.

PCT/IB99/01448

CLAIMS

5

10

15

20

25

30

1. A process for distilling paraffinic hydrocarbons, which process comprises

Fischer-Tropsch derived paraffinic feeding a hydrocarbon feedstock comprising heavy paraffinic optionally, and, light and/or medium hydrocarbons paraffinic hydrocarbons, into a distillation column;

operating the distillation column to produce usable wax products; and

withdrawing from the distillation column an overhead stream, a bottom stream comprising usable wax products, and at least one side stream comprising usable wax products.

- 2. A process according to Claim 1, wherein the Fischer-Tropsch derived paraffinic hydrocarbon feedstock comprises, in addition to the heavy paraffinic hydrocarbons and which comprise hydrocarbon molecules with carbon numbers or carbon atoms in the range C_{15} and greater, also medium paraffinic hydrocarbons comprising hydrocarbon molecules with carbon numbers in the range C_{10} to C_{80} , and light paraffinic hydrocarbons comprising hydrocarbon molecules with carbon numbers in the range C_{35} and less.
- 3. A process according to Claim 2, wherein the operation of the distillation column is such that it produces, as the usable wax products, hard wax comprising hydrocarbon molecules with carbon numbers in the range C_{30} and greater, and medium wax comprising hydrocarbon molecules with carbon numbers in the range C_{20} to C_{38} , with the distillation column also producing paraffins comprising hydrocarbon molecules with carbon numbers in the range C_{23} and less.

15

20

25

30

WO 00/11113 PCT/IB99/01448

4. A process according to any one of Claims 1 to 3 inclusive, wherein the distillation column is operated under vacuum.

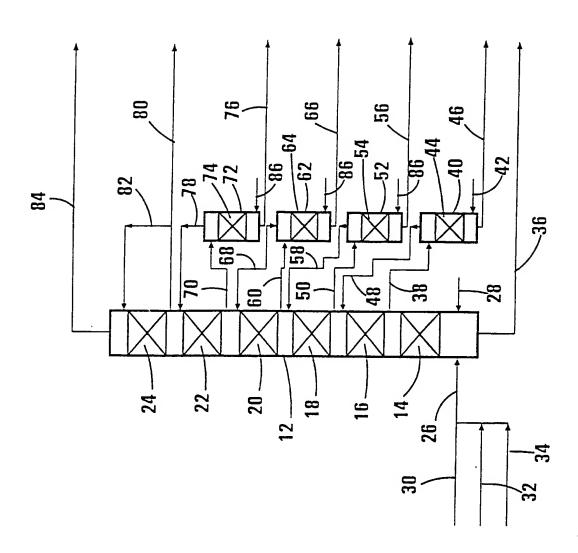
20

- 5. A process according to Claim 4, wherein the distillation column has a sump, with the distillation column being operated such that the pressure in the column is from 1 to 12 mbar(a), and the temperature in the column sump is from 190°C to 350°C, and with the bottom stream being withdrawn from the sump.
- 10 6. A process according to Claim 5, which includes cooling the bottom stream, and recycling up to 10% by volume of the bottom stream to the sump, as a sump quench.
 - 7. A process according to any one of Claim 1 to 6 inclusive, which includes feeding stripping steam into the distillation column, to adjust the relative volatility of components in the feedstock.
 - 8. A process according to any one of Claims 1 to 7 inclusive, wherein the distillation column contains structured packing as a distillation medium, with the structured packing having a surface area (in m^2) to volume (in m^3) ratio of 125:1 to 750:1.
 - 9. A process according to Claim 8, wherein a plurality of the side streams are provided, with the distillation column including a draw point or zone for each of the side streams as well as for the overhead and bottom streams, and with a plurality of distillation stages being provided in the distillation column, with each stage being located between the draw points or zones for two of the streams, and with each stage comprising the structured packing.

21

- 10. A process according to Claim 9, wherein the structured packings of the different stages have the same surface area to volume ratios.
- 11. A process according to Claim 9, wherein the structured packings of at least some of the stages have different surface area to volume ratios.





INTERNATIONAL SEARCH REPORT

Inter onal Application No PCT/IB 99/01448

			101/10 33/01440
A. CLASSI IPC 7	FICATION OF SUBJECT MATTER C10G7/00 C10G73/42		
According to	o International Patent Classification (IPC) or to both national classific	ation and IPC	
B. FIELDS	SEARCHED		
Minimum do IPC 7	ocumentation searched (classification system followed by classification C10G C07C	on symbols)	
Documentat	lion searched other than minimum documentation to the extent that s	such documents are incli	ided in the fields searched
Electronic d	ata base consulted during the international search (name of data bas	se and, where practical	search terms used)
C. DOCUME	ENTS CONSIDERED TO BE RELEVANT		
Category °	Citation of document, with indication, where appropriate, of the rele	evant passages	Relevant to claim No.
А	US 5 486 542 A (POSTHUMA SYTZE A 23 January 1996 (1996-01-23) claims 1-6 column 1, line 26 - line 39	ET AL)	1-5
A	US 2 852 546 A (KOLLING ET AL) 16 September 1958 (1958-09-16) claim 1		1
A	US 2 467 959 A (BOWMAN ET AL) 19 April 1949 (1949-04-19) claims 4-6		1
А	US 1 740 125 A (SULLIVAN) 17 December 1929 (1929-12-17) claims 1-4 		1,4,5,7
Furth	ner documents are listed in the continuation of box C.	X Patent family	nembers are listed in annex.
"A" docume conside "E" earlier of filing de "L" docume which citation "O" docume other n"P" docume	ont defining the general state of the art which is not ered to be of particular relevance tocument but published on or after the international action and the international action of the international action of the stablish the publication date of another or or other special reason (as specified) ent referring to an oral disclosure, use, exhibition or neans	or priority date and cited to understand invention "X" document of particular cannot be consided involve an invention "Y" document of particular cannot be consided document is combinents, such combin the art.	ished after the international filing date into in conflict with the application but dithe principle or theory underlying the lar relevance; the claimed invention red novel or cannot be considered to estep when the document is taken alone lar relevance; the claimed invention red to involve an inventive step when the ined with one or more other such documination being obvious to a person skilled of the same patent family
Date of the a	actual completion of the international search		he international search report
	4 November 1999	02/12/1	999
Name and n	nailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswilk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer De Herd	t, 0

INTERNATIONAL SEARCH REPORT

Information on patent family members

Intc. ional Application No PCT/IB 99/01448

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 5486542	A	23-01-1996	NONE	
US 2852546	A	16-09-1958	NONE	
US 2467959	A	19-04-1949	NONE	
US 1740125	Α	17-12-1929	NONE	